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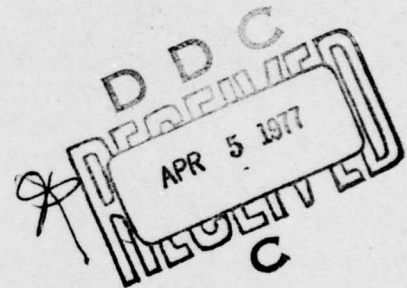
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GROWTH OF PURE SINGLE CRYSTALS OF ALKALI HALIDES AND ALKALINE
EARTH FLUORIDES

Oregon State University
Department of Chemistry



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FOREWORD

This semiannual technical report summarizes work performed by personnel of the Department of Chemistry, Oregon State University, Corvallis, OR 97331, under ARPA Contract No. F19628-76-C-0156. The program was coordinated by Dr. W. J. Fredericks of OSU, and monitored by Major Normantas Kalusutis of RADC/ETSP and Capt. Harry Windsor of ARPA. The report covers the period from 1 March 1976 through 31 August 1976.

SUMMARY

This report covers the initial six months of a program to prepare pure KBr, SrF_2 and BaF_2 single crystals. The work described covers the development of an analytical scheme for determining the effectiveness of various ion exchange resins for the removal of impurities from KBr, and for determining the proper KBr concentrations and pH of these solutions for efficient removal of impurity ions. As these resins very effectively remove aliovalent ions under almost any conditions, the primary problem is to determine those conditions suitable for removal of other alkali metals.

The ion exchange systems which will be completed shortly have been designed to allow maximum flexibility of operating conditions. All parts for the three systems have been fabricated with the exception of the small measuring chambers required for the control of the system, and we are in the process of assembling the first system. The reactive gas manifold for use with the crystal pulling system has been constructed and requires only a few simple monel fittings to be operational. A new seal for the crystal pulling system has been designed in such a way as to prevent even the slightest contamination by ambient laboratory atmosphere. Most of the miscellaneous apparatus required for this program has been assembled in the laboratory.

The work appears to be progressing on schedule and by the next semi-annual report we should have KBr crystals available for measurement of their optical properties.

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I. INTRODUCTION

The purpose of this research is to grow KBr, SrF_2 , and BaF_2 single crystals in two grades of purity. RADC/ETSP will then determine these substances suitability for use as high power laser windows by measuring the absorptivity of these materials by laser calorimetry. That work will determine if the crystals grown from standard grades of KBr, SrF_2 , and BaF_2 under reactive atmospheres are as transparent as crystals of the same substances grown from highly purified salts under similar atmospheres. This semiannual technical report covers the initial six months of this work. During this period many facets of the program were begun but none are as yet finished. This report discusses the progress of each of these as of 31 August 1976.

II. THE DETERMINATION OF ION EXCHANGE RESIN CHARACTERISTICS IN STRONG KBr SOLUTIONS

The initial problem in determining the effectiveness of ion exchange resins in removing undesired alkali metal ions is to develop an analytical scheme capable of sufficient accuracy to determine the effect of the parameters of concentration, pH, and flow rate of solutions through various resins. The analytical method chosen for this work was based on the availability of a Perkin-Elmer Model 403 atomic absorption spectrograph in this laboratory. Because the solution concentration is too large to be used effectively with the atomization burners of the 403, we acquired an HGA 2100 graphite furnace to use as the vaporization device for our

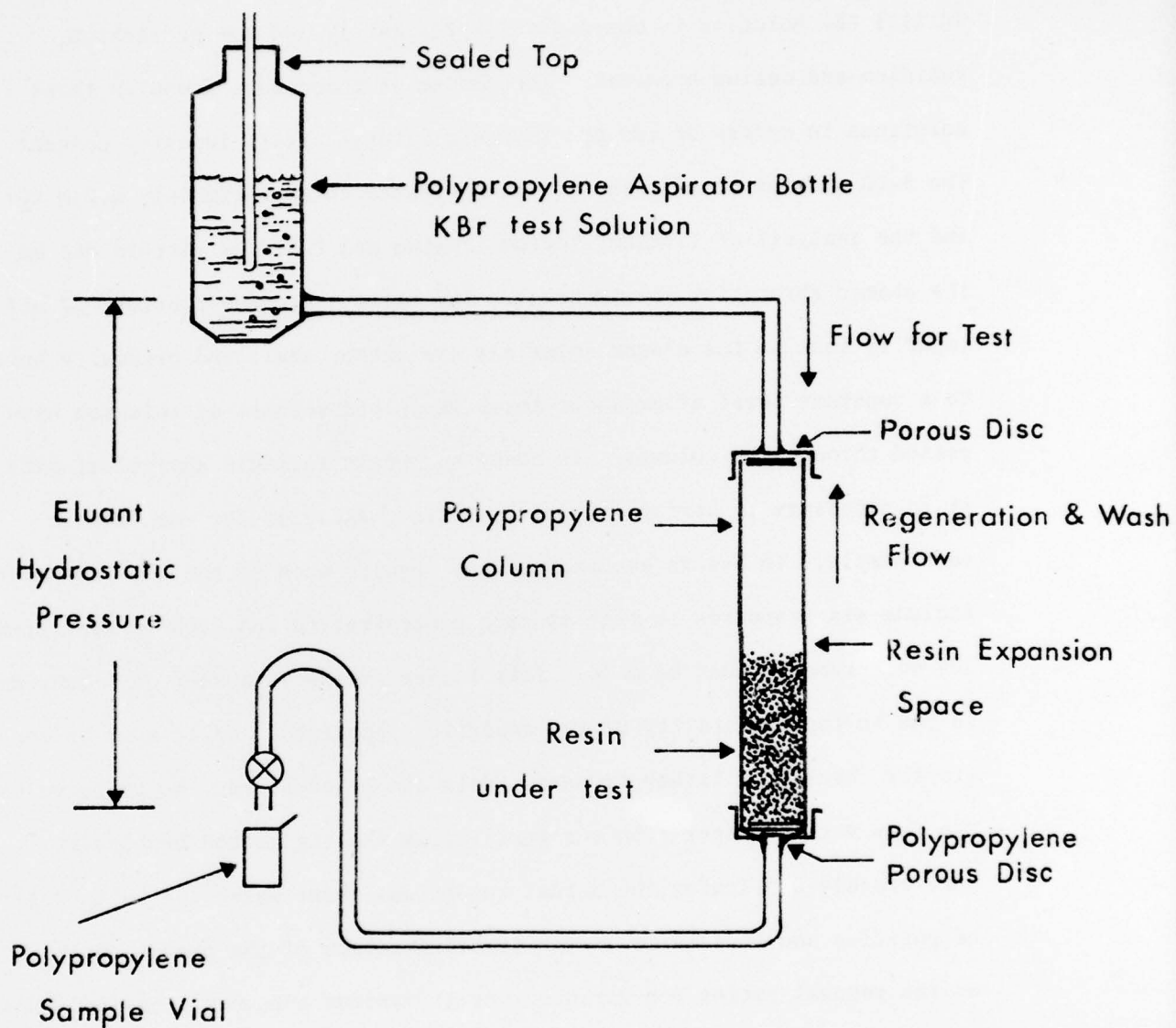
analytical work. A Houston Instrument HF-98 X-YT recorder was modified to operate in synchronization with the graphite furnace control unit. The optics of the Perkin-Elmer 403 were modified with Perkin-Elmer accessory kits to the specifications necessary for this use. Early tests of this apparatus quickly showed that the specifications provided by the Perkin-Elmer company for the analysis of alkali ions do not reflect the true analytical sensitivity for lithium, sodium, cesium or rubidium in KBr solutions. Their specifications apparently represent the analysis of a single ion in a very dilute solution and would not be suitable for an analysis of even sea water, much less more concentrated solutions. This required that we develop techniques suitable for solutions in the concentration range necessary for our studies. This required a considerable expenditure of effort. The conditions under which suitable analyses can be obtained for these ions are given in Table I. The most concentrated solution we can analyze is approximately 0.2 Molar in KBr. With more concentrated solutions we cannot obtain reliable statistics for analytical work. This requires a considerable dilution factor from the solutions actually used in the columns and those analyzed. This, of course, lowers the sensitivity of the device. However, it does offer the advantage that we do not have the clogging burner problems normally associated with analysis at these concentrations with the Perkin-Elmer system.

Once having established the analytical conditions we constructed test columns on a small scale. These consisted of polypropylene columns approximately 20 cm long and 1.5 cm in diameter which contained a porous polypropylene disc at each end supported by a press fit polypropylene

TABLE I. ANALYSIS PROCEDURES FOR ALKALI IONS IN KBr SOLUTIONS

<u>Rubidium</u>	25 mA lamp current		<u>Time</u>	<u>Temp</u>
	$\lambda = 390.0$ - vis (780 nm)			
	Slit = 5 (40 Å)	Dry	10 sec	200°C
	Filter in	Char	20 sec	1000°C
	Recorder response 2	Atomize	15 sec	2100°C
	Quartz windows out			
	1 μ l sample volume			
	No delay time			
	Gas flow 40--normal mode			
	Standards: 0, 1.1, 3, 5, 7, 10 ppm Rb in 0.197 M KBr			
<u>Lithium</u>	12 mA lamp current		<u>Time</u>	<u>Temp</u>
	$\lambda = 335.6$ - vis (671.2 nm)			
	Slit = 5 (40 Å)	Dry	10 sec	200°C
	Filter in	Char	20 sec	1000°C
	Recorder response 2	Atomize	15 sec	2400°C
	Quartz windows out			
	1 μ l sample volume			
	No delay time			
	Gas flow 40--normal mode			
	Standards: 0, 1, 2, 5, 7, 10 ppm Li in 0.197 M KBr			
<u>Cesium</u>	25 mA lamp current		<u>Time</u>	<u>Temp</u>
	$\lambda = 426.1$ - vis (825.2 nm)			
	Slit = 5 (40 Å)	Dry	10 sec	200°C
	Filter in	Char	20 sec	900°C
	Recorder response 2	Atomize	15 sec	2200°C
	Quartz windows out			
	1 μ l sample volume			
	No delay time			
	Gas flow 40--normal mode			
	Standards: 0, 1, 2, 5, 7, 10, 25, 49 ppm Cs in 0.197 M KBr			
<u>Sodium</u>	10 mA lamp current		<u>Time</u>	<u>Temp</u>
	$\lambda = 295$ - vis (590 nm)			
	Slit = 3 (4 Å)	Dry	10 sec	200°C
	Filter out	Char	20 sec	1000°C
	Recorder response 2	Atomize	15 sec	2000°C
	Quartz windows out			
	1 μ l sample volume			
	No delay time			
	Gas flow 40--normal mode			
	Standards: 0, 1, 2, 5, 8, 10 ppm Na in 0.193 M KBr			

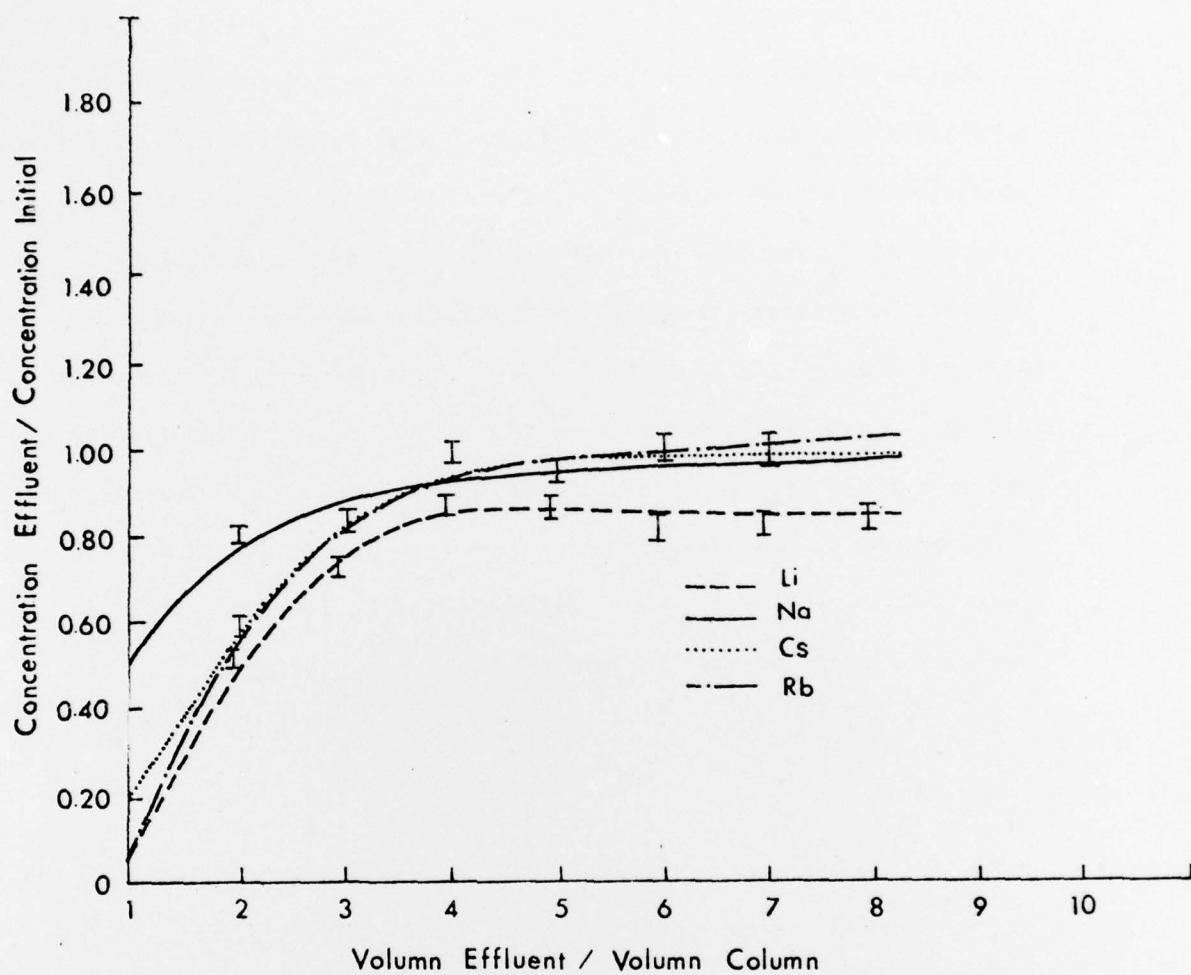
cap with a tube fitting. This test configuration is as shown in Figure 1. The resins are held on the lower porous polypropylene disc in normal operation and the upper disc prevents loss of resin during back flow regeneration and washing. The resins occupy about half the length of the column to allow room for swelling during regeneration. The head is adjusted so that the flow rate is approximately 3 ml of solution per minute. The flow rate scales in proportion to the diameter of the column and was chosen such that the finished columns which are approximately 5 cm in diameter will have an adequate flow rate to obtain reasonable amounts of purified salts in relatively short times. The initial resin tested was Chelex 100 obtained from Bio-Rad Laboratories. These columns are connected to the solution reservoirs and sample collection chamber with Tygon tubing; the sample reservoir is of polypropylene as is the tube establishing the head in the reservoir. Tygon is not the best material choice as it exchanges H^+ for K^+ , but its flexibility is needed. The resins initially arrive in a sodium form. They are converted to the hydrogen form by passing 1 M HBr or HCl in a backflow direction through the column. The hydrogen form is then converted to the potassium form by passing 1 M KOH through the solution in a backflow direction. The conversion is considered complete when at least twice the volume of KOH required for effluent solution pH to approximately equal that of the inflow solution has been passed through the column. At this point the direction of flow is reversed and the KBr solution to be purified is passed through the column. The dead volume of the column and its associated connecting tubing is measured and this amount of solution is discarded.



Test Apparatus

Figure 1: Resin Test Column

Then KBr at a specified concentration and pH is passed through the column. Eight to ten 10-ml samples of each solution are collected. The initial KBr solution is doped with approximately 100 ppm of lithium, rubidium and cesium bromides. The amount of these ions found in these solutions in excess of 100 ppm is their natural alkali impurity content. The 8-10 samples of effluent are then diluted to approximately 0.2 N KBr and the analysis of lithium, sodium, cesium and rubidium carried out on the atomic absorption spectrograph. Initially the concentrations of all impurity ions in the eluant solutions are rather small and gradually build to a constant level after about three resin bed volumes of solution have passed through the columns. In order to obtain reliable analytical data, it is necessary to perform from 3-5 separate analyses for each ion in each sample. To assure accuracy of the results each of the analyses must include six standards so that at each concentration and each pH approximately 224 measurements must be made. This rather excessive number of measurements is due to the instability of the analytical apparatus and it must be constantly checked or rather erroneous data can be obtained. We chose to use the flow method rather than the equilibrium shaking method because it more closely duplicates the actual conditions under which the salts will be purified and thus tells us the time dependence of the process as well as the removal ratios for various ions at various concentrations and pH's. To date we have covered the range from 4 Molar to 1 Molar in half-Molar steps, and the pH range from 9 to 5. Figure 2 shows a typical plot of the ratio of the impurity in the effluent to the impurity in the original solution as a function of the number of volumes of resin bed of solution



KBr 4.055M: PH 4.91 FLOW RATE 3ml/Min: Column 4

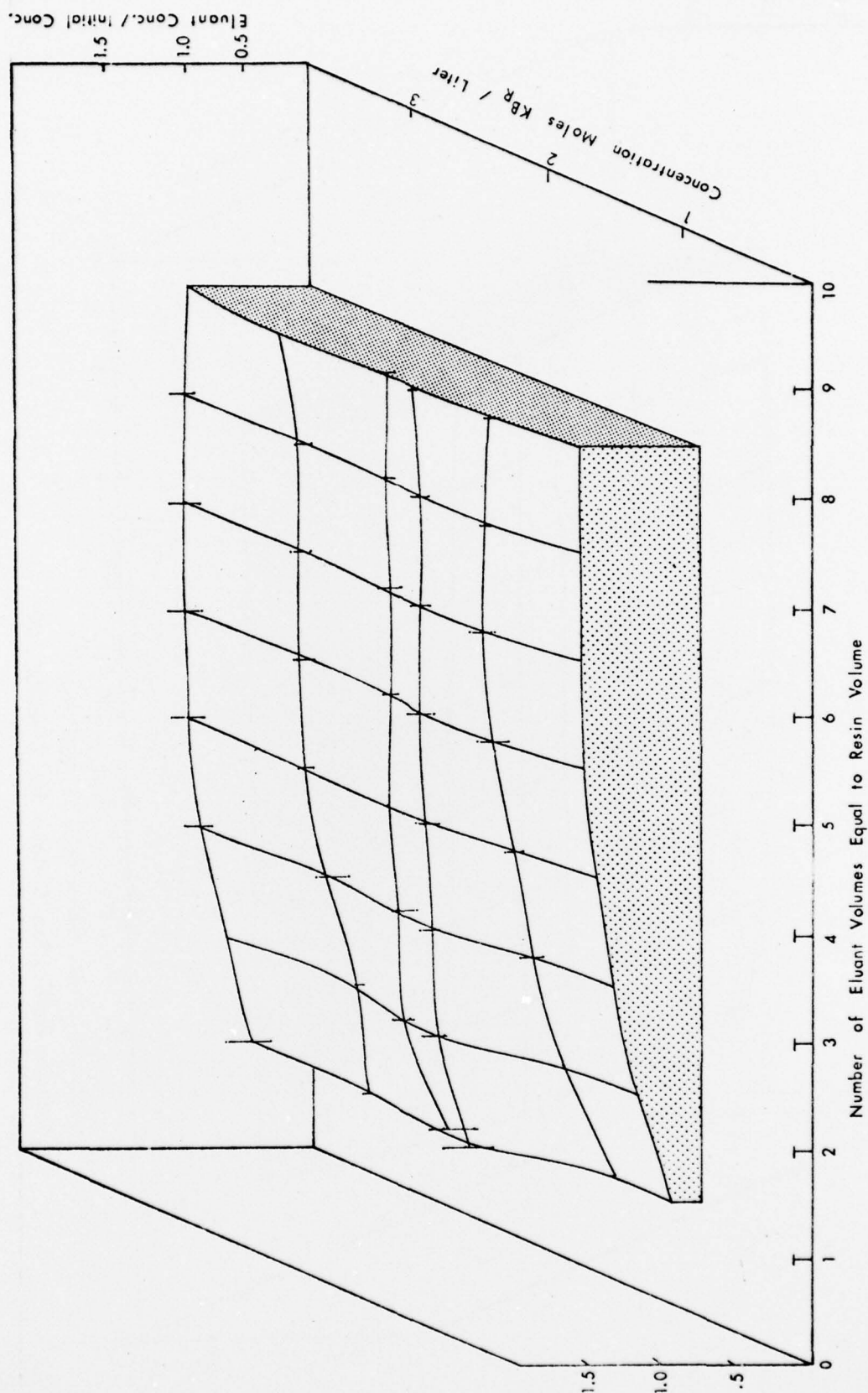
Initial Concentrations (ppm): Li 160: Na 41.8: Cs 710: Rb 291

Figure 2: Removal Ration C_E/C_i vs. Volume V_E/V_{Resin}

passed through the column. Figure 3 shows the variation of selectivity for all of the alkali ions as a function of concentration. Similar data is gathered for each pH and from this the optimum operating range for the resin in terms of the amount of purified salt produced per unit time at a purification ratio acceptable for this work is determined. The final operating conditions must be obtained from the full sized system. These measurements give the basic region useful in these purifications. At present the work on Chelex 100 is nearly complete and the work on a resin designated as AG-50W-X8 is well underway. We have yet to investigate Bio-Rex 40 and Bio-Rex 70. The measurements at each concentration and pH for each resin are run in duplicate. Chelex 100 will be the resin in our first column of the purification system. We anticipate that a bed approximately 43 cm long and 5 cm in diameter will be adequate to reduce our impurities to an acceptable level.

III. THE ION EXCHANGE SYSTEMS

The ion exchange system for purification of KBr is a seven-column system. Those for the purification of SrF_2 and BaF_2 are nine-column systems. These have been designed to allow maximum flexibility of operating conditions. The systems are rather complex and the simplest, KBr, alone involves 55 valves and 10 measuring chambers to determine the conditions of the operation. The systems must be constructed of materials that have been proven not to contribute contamination to the salt. These include methacrylate, polypropylene, and teflon, and polypropylene-



Lithium Purification Surface for CHELEX 100

Figure 3a: Removal Ratio C_E/C_i vs. KBr Solution Concentration

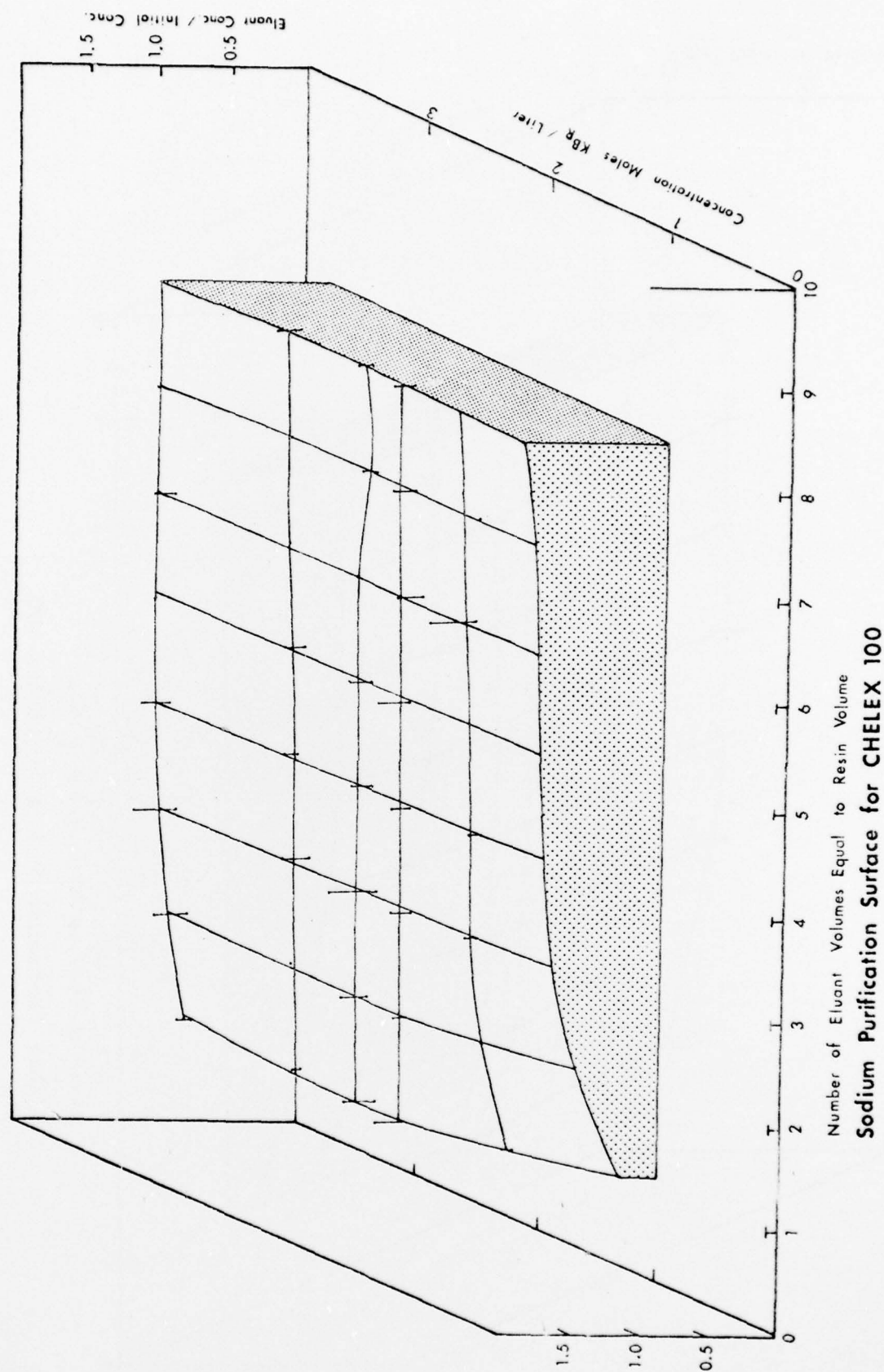
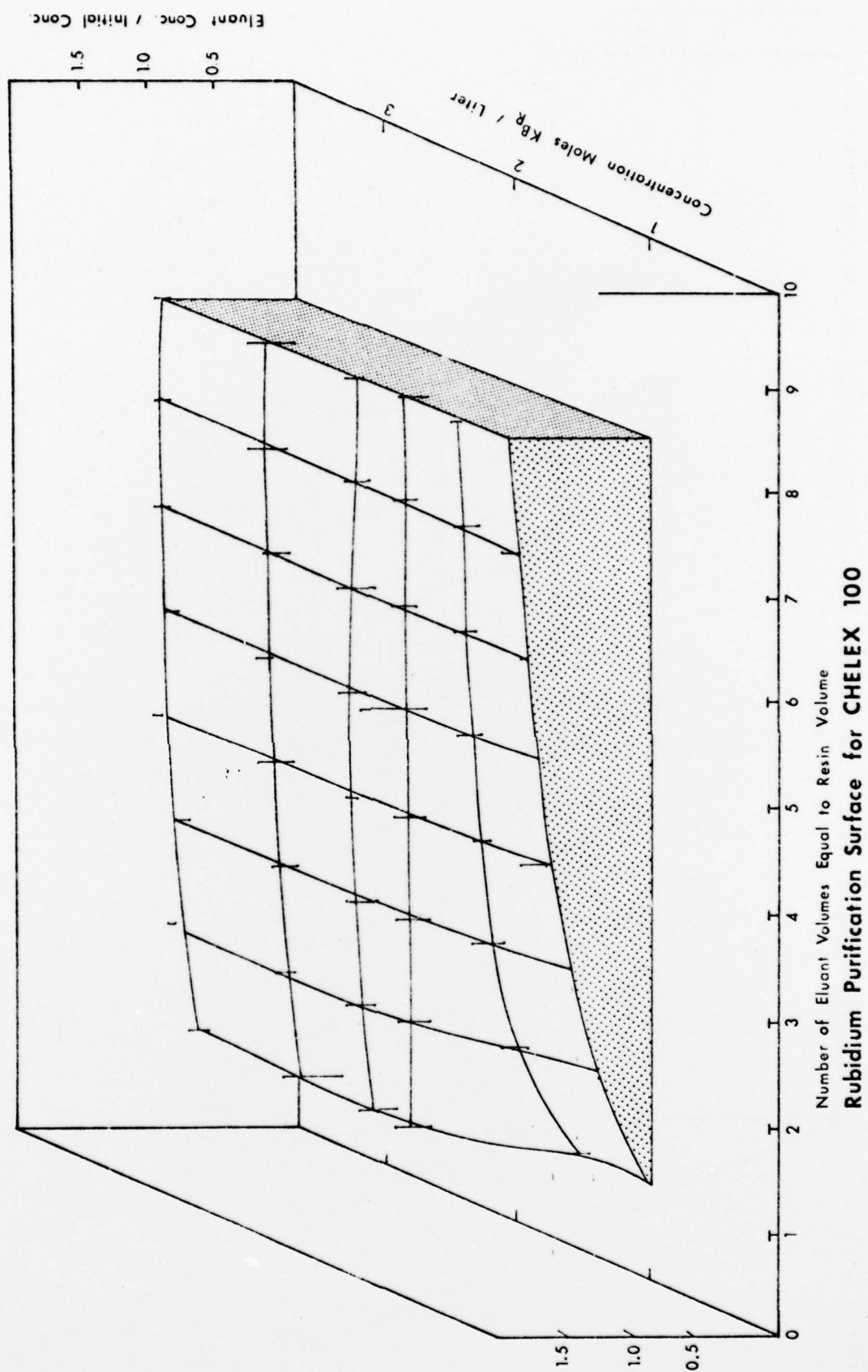


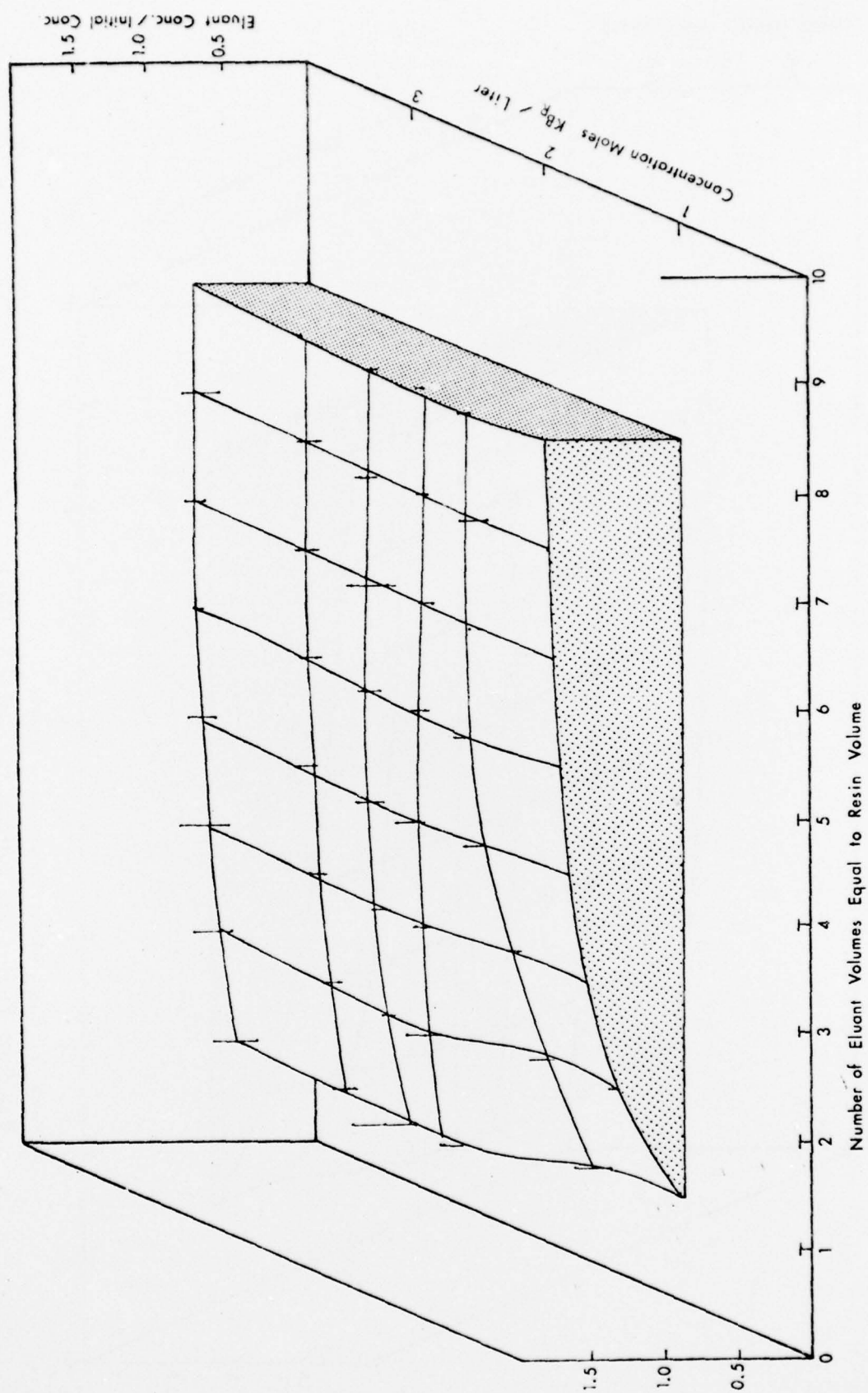
Figure 3b: Removal Ratio C_E/C_i vs. KBr Solution Concentration
 Sodium Purification Surface for CHELEX 100

Number of Eluant Volumes Equal to Resin Volume



Rubidium Purification Surface for CHELEX 100

Figure 3c: Removal Ratio C_E/C_i vs. KBr Solution Concentration



Cesium Purification Surface for CHELEX 100

Figure 3d: Removal Ratio C_E/C_i vs. KBr Solution Concentration

polyethylene o-rings for those parts not contacting the regeneration solution KOH. For KOH we use a new soft teflon o-ring rather than the polypropylene-polyethylene. All parts for these three systems have been fabricated with the exception of the measuring chamber. Its exact design depends on the size of the detecting elements that we use. At present we are having some difficulty finding fast enough pH electrodes for use with this system. Glass electrodes operate with an acceptable rate of response; however, we would prefer one of the more durable electrodes presently available. That particular component is of rather simple construction and so will not be a major problem in fabrication. While the system scheme is as shown in the original proposal, the final lay-out of the board containing the ion exchange system has not been completed. A picture or drawing will be included in the next semiannual report.

IV. REACTIVE GAS MANIFOLD

The reactive gas system is shown in Figure 4. It is a completely greaseless system as no grease exists that will withstand the gases used in preparation of pure KBr without the production of volatile products that eventually end up in the crystal. A portion of the manifold is constructed of glass and teflon-glass valves. This portion is used for distillation and purification of HBr, Br₂, HCl and Cl₂. The remainder of the system consists of the initial inert gas flushing necessary to avoid excessive corrosion in the metallic parts, nickel or monel, of the system, the vacuum manifold, and the system for supplying reactive gases at various pressures. The remainder of the connections assure safety in case of

Multistage Reactive Gas Seal

Materials: All Metal Nickel

All O-Rings DuPont Perfluoroelastomer

All Internal O-Ring Supports Teflon

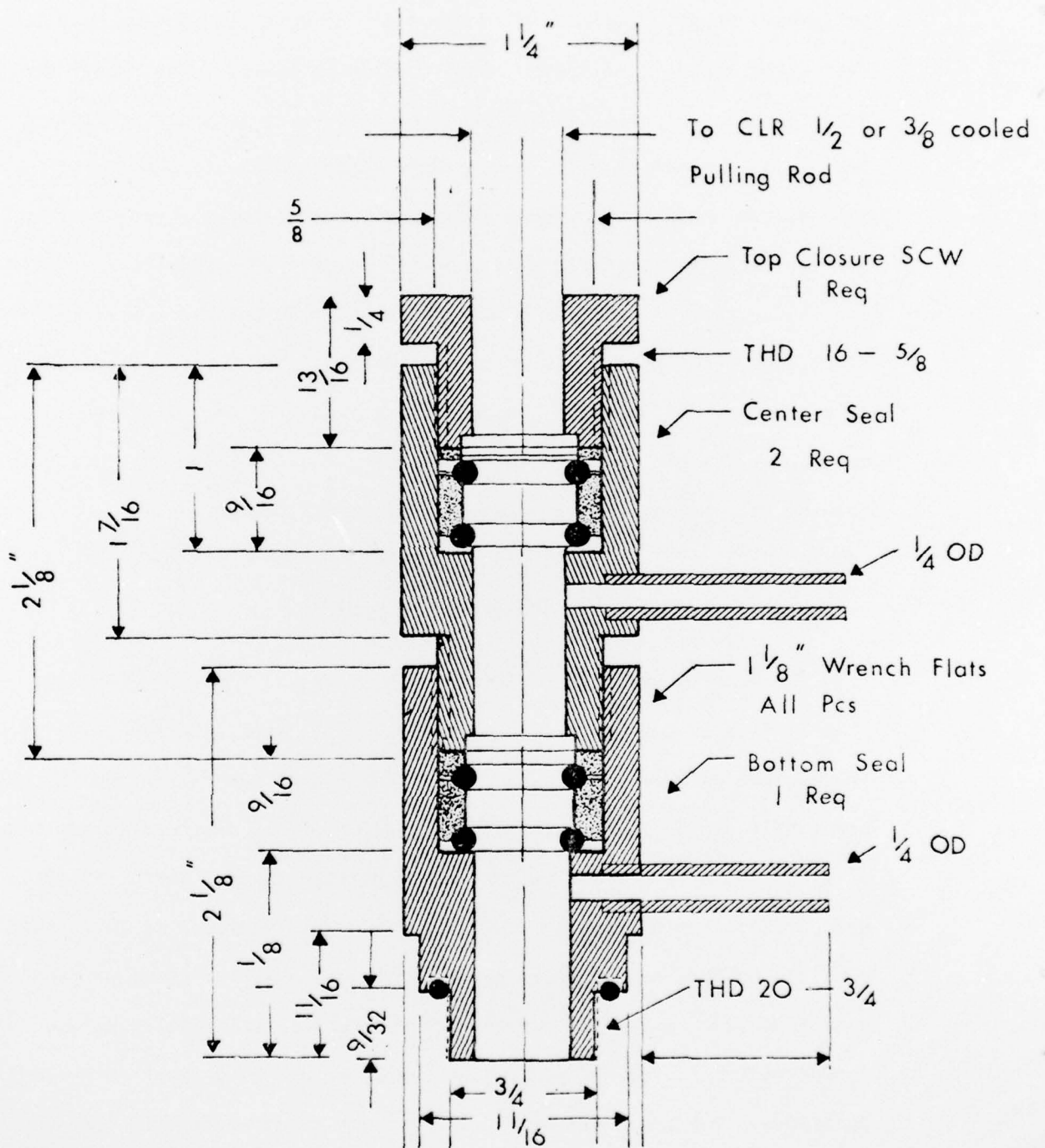


Figure 4: Reactive Gas System

failure of various components of the system, and a safe dump for the toxic gases. The system is straightforward and manufactured of relatively standard components and needs little further discussion. The drawing should provide the necessary information on any of the components of the system.

Our method of growing crystals is to pull from a melt. This means that we must have a rotating seal that will permit linear motion of the water cooled pulling rod. It should further be noted that to grow good crystals of alkali halides, the pressure in the quartz growing chamber must be considerably below one atmosphere. Otherwise entrapment of the reactive gas in the crystal can occur. This low pressure means that unless special precautions are taken there will be a leakage of the ambient atmosphere of the laboratory into the growth chamber. This can cause contamination of the crystal by OH^- . However, a pulled crystal is considerably superior to that grown in an enclosed container with regard to internal strain in the crystal. To allow us to pull crystals and avoid the ambient atmosphere contamination or the entrapment of gas within the crystal, we have designed a three-stage seal. The initial seal is pumped at the same pressure and under the same atmosphere as the growth chamber. The second stage of the seal contains the reactive gas at a pressure slightly above atmospheric. The third stage of the seal contains argon at a pressure slightly above that of the second stage. Thus the small leakage around the seal allows argon to escape into the room; should the second stage leak, it will leak argon rather than air; and in the third stage, the leakage from the high-pressure reactive gas seal can

contain at most a trace of argon but mostly reactive gas which will be evacuated on the pumping line from the first stage of the seal. Thus we avoid contamination of the growing chamber atmosphere with undesirable components of the atmosphere. Figure 5 shows the basic design of the seal.

V. MISCELLANEOUS OPERATIONS DURING THIS QUARTER

Suitable racks for holding the ion exchange systems and for holding the solution reservoirs have been constructed. A high purity water system, Millipore Milli-Q II, has been installed and is operational and of course provides the water for our analytical work. Our safety committee is requiring the installation of an exhaust system in case of failure of any of our toxic gas systems. This is a simple modification and is being constructed at present. The systems for vacuum evaporation of the solutions from the columns have arrived. These consist of simple vacuum ovens and a pumping system capable of removing large quantities of water without recontamination of the salt.

VI. CONCLUSIONS

At this stage definite conclusions are premature. At present it appears that the KBr system will function as proposed. The ion exchange resins do not differ in their behavior with respect to solutions of high ionic strength any more than expected. As usual the selectivities decrease as the concentration increases but we can still handle at least 1.5 M KBr which will be adequate to obtain substantial amounts of salt

Schematic of Greaseless Manifold for Corrosive Gas Treatment

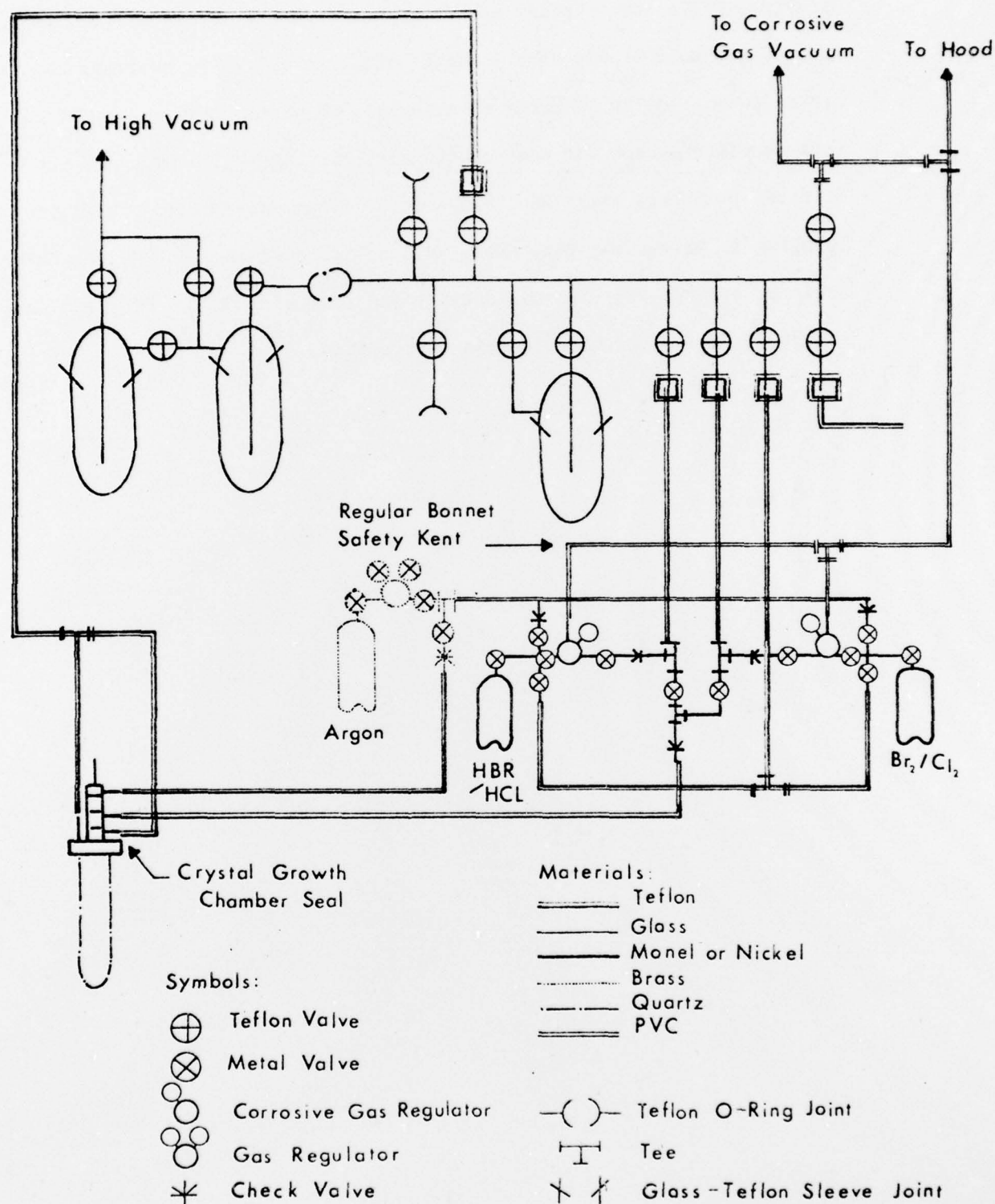


Figure 5: Reactive Gas Crystal Growth System Seal

easily. While the fabrication of the ion exchange column systems is proceeding more slowly than I anticipated, it is making progress and there is no serious delay in terms of materials or parts. The gas manifolds are complete except for some minor monel fittings which have not yet arrived. At this stage of the operation I can only conclude that the program is proceeding reasonably well on schedule and that we should be able to produce KBr crystals shortly and that work on the SrF_2 and BaF_2 exchange systems should progress on schedule.

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